

AD-A231 237

DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution list enclosed		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 26			5 MONITORING ORGANIZATION REPORT NUMBER		
6a NAME OF PERFORMING ORGANIZATION State University of New York at Buffalo		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry Buffalo, NY 14214			7b ADDRESS (City, State, and ZIP Code) Department of the Navy 800 North Quincy Street Arlington, VA 22217		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1530; R&T Code 4135002		
8c ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO 4135002
11 TITLE (Include Security Classification) Diphenylphosphide Derivatives of Bisneopentylgallium and -indium. Crystal and Molecular Structures of $[(Me_3CCH_2)_2GaPPh_2]_2$ and $[(Me_3CCH_2)_2InPPh_2]_3$.					
12 PERSONAL AUTHOR(S) Michael A. Banks, G.T. Beachley, Jr., Lisa A. Buttrey, Melvyn Rowen Churchill and James C. Fettingner					
13a TYPE OF REPORT Technical Report		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year, Month, Day) 18 January 1991	
				15 PAGE COUNT 32	
16 SUPPLEMENTARY NOTATION To be published in <u>Organometallics</u>					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Organogallium and indium compounds, gallium- and indium-phosphorus compounds X-ray structural study.		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) The two compounds, $(Me_3CCH_2)_2MPPh_2$ (M=Ga, In), have been prepared by metathetical reactions between $(Me_3CCH_2)_2MCl$ and $KPPh_2$ and fully characterized. The characterization data include elemental analyses (C,H), melting points, IR, 1H and ^{31}P NMR spectral studies, cryoscopic molecular weight studies in benzene solution and single crystal X-ray structural studies. The gallium compound exists as a dimer in benzene solution and in the solid state. The corresponding indium derivative exists as a monomer-dimer equilibrium mixture in benzene solution and as a trimer in the solid state. Thus,					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL O.T. Beachley, Jr.			22b TELEPHONE (Include Area Code) 716-831-3266		22c OFFICE SYMBOL

$(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ represents an unusual example of an amphoteric compound which exhibits three different degrees of association.

$[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ crystallizes in the monoclinic space group $P2_1/n$ [No. 14] with $a = 11.076(3)$, $b = 18.996(3)$, $c = 21.753(5)\text{\AA}$, $\beta = 100.128(9)$, $V = 4505(2)\text{\AA}^3$ and $Z = 4$ (dimeric molecules). The molecule contains a buckled Ga_2P_2 core (dihedral angles of 142.2° across $\text{P}(1)\cdots\text{P}(2)$ and 145.6° across $\text{Ga}(1)\cdots\text{Ga}(2)$); Ga-P distances are in the range $2.479(3)$ – $2.512(3)\text{\AA}$ and Ga-C(neopentyl) bond lengths are in the range $1.996(12)$ – $2.016(12)\text{\AA}$.

$[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148); unit cell parameters (hexagonal setting) are $a = 20.873(5)$, $c = 29.037(4)\text{\AA}$, $V = 10.956(4)\text{\AA}^3$ and $Z = 6$ (trimeric molecules). The molecules lie on sites of C_3 symmetry, their In_3P_3 cores having a chair conformation. The independent In-P distances are $2.677(1)$ and $2.699(2)\text{\AA}$; In-C(neopentyl) bond lengths are $2.182(6)$ and $2.210(7)\text{\AA}$.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

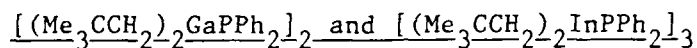
OFFICE OF NAVAL RESEARCH

Contract N-00014-90-J-1530

R&T Code 4135002

TECHNICAL REPORT NO. 26

Diphenylphosphide Derivatives of Bisneopentyl-
gallium and -indium. Crystal and Molecular Structures of



by

Michael A. Banks, O. T. Beachley, Jr., Lisa A. Buttrey,

Melvyn Rowen Churchill and James C. Fettingner

Prepared for Publication

in

Organometallics

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14214

18 January 1991

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

Contribution from the Department of Chemistry,
State University of New York at Buffalo,
Buffalo, N.Y. 14214

Diphenylphosphide Derivatives of Bisneopentyl-
gallium and -indium. Crystal and Molecular Structures of
 $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ and $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

by

Michael A. Banks, O. T. Beachley, Jr.^{*}, Lisa A. Buttrey,
Melvyn Rowen Churchill^{*} and James C. Fettingner

Abstract

The two compounds, $(\text{Me}_3\text{CCH}_2)_2\text{MPPh}_2$ (M=Ga, In), have been prepared by metathetical reactions between $(\text{Me}_3\text{CCH}_2)_2\text{MCl}$ and KPPh_2 and fully characterized. The characterization data include elemental analyses (C,H), melting points, IR, ^1H and ^{31}P NMR spectral studies, cryoscopic molecular weight studies in benzene solution and single crystal X-ray structural studies. The gallium compound exists as a dimer in benzene solution and in the solid state. The corresponding indium derivative exists as a monomer-dimer equilibrium mixture in benzene solution and as a trimer in the solid state. Thus, $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ represents an unusual example of an amphoteric compound which exhibits three different degrees of association.

$[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ crystallizes in the monoclinic space group $\text{P}2_1/\text{n}$ [No. 14] with $a = 11.076(3)$, $b = 18.996(3)$, $c = 21.753(5)\text{\AA}$, $\beta = 100.128(9)$, $V = 4505(2)\text{\AA}^3$ and $Z = 4$ (dimeric molecules). The molecule contains a

buckled Ga_2P_2 core (dihedral angles of 142.2° across $\text{P}(1)\cdots\text{P}(2)$ and 145.6° across $\text{Ga}(1)\cdots\text{Ga}(2)$); Ga-P distances are in the range $2.479(3)$ - $2.512(3)\text{\AA}$ and Ga-C(neopentyl) bond lengths are in the range $1.996(12)$ - $2.016(12)\text{\AA}$.

$[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148); unit cell parameters (hexagonal setting) are $a = 20.873(5)$, $c = 29.037(4)\text{\AA}$, $V = 10.956(4)\text{\AA}^3$ and $Z = 6$ (trimeric molecules). The molecules lie on sites of C_3 symmetry, their In_3P_3 cores having a chair conformation. The independent In-P distances are $2.677(1)$ and $2.699(2)\text{\AA}$; In-C(neopentyl) bond lengths are $2.182(6)$ and $2.210(7)\text{\AA}$.

Introduction

The formation of group 13-15 materials such as GaAs and InP from single source precursors of the type $R_2MER'_2$ (M = group 13 element, E = group 15 element)¹ has provided the motivation to understand more fully the chemistry of this class of compounds. Since the most desirable compounds for preparing group 13-15 materials by organometallic chemical vapor deposition (OMCVD) are volatile liquids, our goal has been to study the factors which control the degree of association of these Lewis amphoteric species, their structures and their physical properties. Some representative examples of monomers are $(C_5Me_5)_2GaAs(SiMe_3)_2$ ² and $t-Bu_2GaAsBu^t_2$,³ of dimers are $[Me_2GaPBu^t_2]_2$ ⁴ and $(Me_2InPBu^t_2)_2$ ⁵ and $[(Me_3SiCH_2)_2InPPh_2]_2$,⁶ of trimers are $[Et_2GaPEt_2]_3$ ⁷ and $[Cl_2GaAs(CH_2SiMe_3)_3]_3$.⁸ These examples might suggest that steric effects provide an important factor for controlling the degree of association. However, other factors⁹ including valency angle strain, mechanism of formation and solvation effects might also be significant. It is noteworthy that most dimers have planar rings but examples with puckered rings have been observed also. In the case of trimers, planar, boat, twist-boat and irregular boat structures have been observed. Apparently, these rings involving group 13-15 elements are sufficiently flexible to accommodate a variety of different conformations.

In this paper we report the synthesis and characterization of $(Me_3CCH_2)_2GaPPh_2$ and $(Me_3CCH_2)_2InPPh_2$. Neopentyl group 13 derivatives are of interest because $In(CH_2CMe_3)_3$ has been used to make InP and InSb of electronic quality by OMCVD.^{10,11} The new group 13-15 compounds were synthesized by metathesis reactions. The characterization data include elemental analyses (C,H), melting points, 1H and ^{31}P NMR spectral studies, cryoscopic molecular weight studies and single crystal X-ray structural

studies. The gallium derivative exists as a dimer in benzene solution and in the solid phase. In contrast, the indium compound is a monomer-dimer equilibrium mixture in benzene solution whereas a trimer is observed in the crystalline phase.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and water and were manipulated in a standard vacuum line or in a purified argon atmosphere. All solvents were purified before use. Bisneopentylgallium chloride¹² and bisneopentylindium chloride¹³ were prepared as previously described. Diphenylphosphine was purchased from Strem Chemicals, Inc. and was purified by distillation prior to use. Potassium diphenylphosphide¹⁴ (KPPh₂) was prepared from diphenylphosphine and excess KH in diethyl ether. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak) and sh (shoulder). The ¹H NMR spectra were recorded at 90MHz by using a Varian Model EM-390 spectrometer. All samples for NMR spectra were contained in sealed NMR tubes. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe₄ as δ 0.00 and benzene as δ 7.13. The ³¹P NMR spectra were recorded at 36.23 MHz by using a JEOL FX-90Q spectrometer. The proton decoupled spectra are reported relative to 85% H₃PO₄ as δ = 0.00 ppm. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdson.¹⁵

Synthesis of (Me₃CCH₂)₂GaPPh₂. The compound (Me₃CCH₂)₂GaPPh₂ was synthesized by a methathesis reaction by using 0.804 g (3.58 mmol) of KPPh₂ and 0.888 g (3.59 mmol) of Ga(CH₂CMe₃)₂Cl in 50 mL Et₂O. The KPPh₂ was added to the solution of Ga(CH₂CMe₃)₂Cl at -78°C and then the mixture was allowed to warm to room temperature. After the solvent had been removed by vacuum distillation, the product was separated by extraction with pentane. The pentane insoluble off-white solid (0.192 g, 2.58, 71.9% KCl) was

isolated from the frit. The colorless pentane soluble solid was identified as $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$ (1.347 g, 3.391 mmol, 94.7% based on KPPh_2). Colorless crystals of $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$ (0.866 g, 2.18 mmol, 60.8% based on KPPh_2) were obtained by slow crystallization from a saturated pentane solution maintained at 20°C. Crystallographic quality crystals were obtained from a saturated methylcyclohexane solution maintained at -15°C.

$(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$. mp 157-160°C dec (glass transition, 132-135°C). ^1H NMR (C_6H_6 , δ): 1.10 (s, 18 H, $-\text{CMe}_3$), 1.39 (t, $^3J_{\text{PGaCH}} = 3.6$ Hz, 4.2 H, $-\text{CH}_2-$). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$, δ): -25.9 (s, 0.024-0.403 molal). Anal. Calcd.: C, 66.52; H, 8.14. Found: C, 66.83; H, 8.08. Cryoscopic molecular weight, formula weight 397.23 (calculated molality, observed molality, association): 0.07568, 0.0337, 2.25; 0.06626, 0.0299, 2.21; 0.06346, 0.0290, 2.19; 0.04326, 0.0199, 2.18. IR (Nujol mull, cm^{-1}): 3070 (w), 3050 (w), 1942 (vw), 1870 (vw, br), 1800 (vw, br), 1580 (w), 1430 (s), 1354 (s), 1328 (vw), 1300 (vw), 1265 (vw), 1234 (m), 1220 (m), 1175 (vw), 1165 (vw), 1152 (w), 1140 (w), 1131 (w), 1128 (w), 1109 (w), 1102 (w), 1098 (w), 1090 (w), 1065 (w), 1021 (m), 1010 (w), 995 (m), 976 (vw), 960 (vw), 928 (vw), 905 (vw), 886 (vw), 839 (vw), 740 (m), 730 (s), 718 (m), 710 (m), 688 (vs), 675 (m, sh), 602 (m), 580 (vw), 540 (vw), 510 (m), 502 (m), 469 (w), 462 (w), 450 (w), 385 (w), 285 (vw).

Synthesis of $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$. The compound $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ was synthesized from 0.538 g (1.84 mmol) of $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ and 0.412 g (1.84 mmol) of KPPh_2 . The indium containing product (0.499 g, 1.13 mmol, 61.5% yield based on $\text{In}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$) was isolated by benzene extraction. Crystallographic quality crystals were obtained by heating a saturated solution to 35°C and then permitting the solution to slowly cool to room temperature. The characterization data for the compound prepared by the

metathetical reaction as described above were similar to the data reported for the compound prepared by the elimination reaction⁶ between $\text{In}(\text{CH}_2\text{CMe}_3)_3$ and $\text{P}(\text{H})\text{Ph}_2$.

Collection of X-Ray Diffraction Data for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$. A fragment of approximate size 0.7 x 0.6 x 0.4 mm was cut from a larger crystal and sealed into a thin-walled glass capillary; these manipulations were performed under an inert atmosphere (Ar). The capillary was mounted in a brass pin on a eucentric goniometer and was accurately centered on a Syntex P2₁ automated four-circle diffractometer. All subsequent operations (determination of orientation matrix and cell parameters, and data collection) were carried out as described previously.¹⁶ Details are presented in Table 1.

The crystal belongs to the monoclinic system (2/m diffraction symmetry). The systematic absences ($h0l$ for $h+l = 2n+1$ and $0k0$ for $k = 2n+1$) uniquely define the centrosymmetric monoclinic space group $\text{P}2_1/n$ (a common variant of $\text{P}2_1/c$, No. 14). All data were corrected for decay (linear correction for an ~30% decrease in intensities of the standard reflections), absorption, and Lorentz and polarization factors and were placed on an approximately absolute scale by means of a Wilson plot.

Solution and Refinement of the Structure of $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$. All crystallographic calculations were carried out under our locally modified set of Syntex XTL programs. Calculated structure factors were based upon the analytical functions expressing scattering factors for neutral atoms.¹⁷ Both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion¹⁸ were included for all non-hydrogen atoms. The function minimized in least-squares refinement was $\sum w(\Delta F)^2$ where $w = \{[o(|F_o|)]^2 + [0.015|F_o|]^2\}^{-1}$. Discrepancy indices are defined as follows:

$$R_F(\%) = 100 \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$R_{wF}(\%) = 100 [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$$

$$GOF = [\Sigma w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$$

Here, NO is the number of observations and NV is the number of variables.

The structure was solved by use of MULTAN¹⁹ which revealed the positions of the heavy atoms. The remaining non-hydrogen atoms were located from a difference-Fourier map. Refinement of positional and thermal parameters (anisotropic for the $[(C_3C-C)_2GaP_2]_2$ moiety and isotropic for carbon atoms of the phenyl groups) and with hydrogen atoms in idealized locations²⁰ led to convergence with $R_F = 5.7\%$, $R_{wF} = 7.7\%$ and $GOF = 1.60$ for data with $|F_o| > 6\sigma(|F_o|)$ [$R_F = 10.8\%$ and $R_{wF} = 9.3\%$ for all data]. We attribute these rather high values to crystal decomposition in the X-ray beam.

A final difference-Fourier map showed no unexpected features ($\rho(\max) = 0.47 \text{ e}^-/\text{\AA}^3$). Final positional parameters are given in Table 2.

Collection of X-Ray Diffraction Data for $[(Me_3CCH_2)_2InP_2]_3$. A clear colorless parallelepiped of dimensions $0.5 \times 0.3 \times 0.25 \text{ mm}$ was sealed (under Ar) into a capillary and mounted as for the previous study (vide supra). Crystal data are compiled in Table 1.

The crystal is rhombohedral, with $\bar{3}$ symmetry (rather than $\bar{3}m$). In the triply-primitive obverse hexagonal setting, the only systematic absences are for $-h+k+l \neq 3n$. Possible space groups are the non-centrosymmetric $R\bar{3}$ [C_3 ; No. 146] or the centrosymmetric $R\bar{3}$ [C_{3i} , No. 148].²¹ The latter is more probable with $Z = 6$ (trimeric units) and was confirmed by the successful solution in this higher-symmetry space group. Data for three equivalent forms were collected. Following correction for absorption, these were

merged to a unique set ($R(I) = 3.1\%$), were corrected for Lorentz and polarization factors and were placed on an approximately absolute scale by means of a Wilson plot. Intensity statistics were in keeping with the centric case.

Solution and Refinement of the Structure of $[(Me_3CCH_2)_2InPPh_2]_3$. The structure was solved by means of a Patterson synthesis, which revealed the location of the crystallographically unique indium atom. Difference-Fourier syntheses led to the location of all non-hydrogen atoms and most hydrogen atoms. Full-matrix least squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms, with all hydrogen atoms included in idealized locations²⁰ ($d(C-H) = 0.95\text{\AA}$, staggered tetrahedral or externally-bisecting trigonal geometry), led to convergence with $R_F = 4.6\%$, $R_{wF} = 5.3\%$ and $GOF = 1.21$ for all 3214 data [$R_F = 3.2\%$, $R_{wF} = 4.9\%$ for those 2436 data with $|F_o| > 6\sigma(|F_o|)$].

A final difference-Fourier was essentially featureless ($\rho(\max) = 0.40\text{ e}^-/\text{\AA}^3 \sim 0.6\text{\AA}$ from In). Positional parameters are collected in Table 3.

Lewis Acidity-Basicity Studies of $(Me_3CCH_2)_2GaPPh_2$. Phosphorus-31 NMR spectroscopy was used to investigate the Lewis acidity-basicity studies of $(Me_3CCH_2)_2GaPPh_2$ towards Et_2O , THF and NMe_3 and $Ga(CH_2CMe_3)_3$. No stable (isolable) adducts could be isolated at room temperature. The only reagent which produced spectroscopic data indicative of a Lewis acid-base interaction was NMe_3 . All other reagent combinations provided ^{31}P NMR spectra which had a line at -25.1 ppm indicative of $[(Me_3CCH_2)_2GaPPh_2]_2$. When an aliquot of a solution prepared by combining 0.137 g (0.346 mmol) of $(Me_3CCH_2)_2GaPPh_2$, 0.211 g (3.57 mmol) of NMe_3 and 4 mL of C_6H_6 was studied, lines were observed at -25.1 ppm (s, 4.21) and at -43.7 ppm (s, 1.00). Removal of NMe_3 and C_6H_6 from the remainder of original solution afforded a

colorless solid whose solution in benzene exhibited only one line at -25.1 ppm, $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$, in the ^{31}P NMR spectrum.

Results and Discussion

The two compounds, $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$ and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$,⁶ have been prepared by metathetical reactions from the appropriate neopentylmetal halide derivative and KPPH_2 and have been fully characterized. The characterization data include elemental analyses, cryoscopic molecular weight measurements in benzene solution, IR, ^1H and ^{31}P NMR spectroscopic data and single crystal X-ray structural studies. The indium derivative was previously described⁶ but an X-ray structural study was not reported. It is noteworthy that the gallium compound is dimeric in the solid state and in benzene solution. In contrast, the indium derivative is trimeric in the crystalline state, but a monomer-dimer equilibrium mixture in benzene solution.

Crystals of bisneopentylgallium diphenylphosphide are composed of discrete dimeric units of composition $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$, which are mutually separated by normal van der Waal's distances. Distances and angles are provided in Tables 4 and 5. An ORTEP diagram, showing atomic labelling, is illustrated in Figure 1. Rather surprisingly, the dimeric molecule has a buckled or butterfly ring geometry rather than a planar Ga_2P_2 core. (There is no crystallographic symmetry imposed upon the molecule). The dihedral angles are: $\text{Ga}(1)\text{-P}(1)\text{-Ga}(2)/\text{Ga}(1)\text{-P}(2)\text{-Ga}(2) = 142.2^\circ$ and $\text{P}(1)\text{-Ga}(1)\text{-P}(2)/\text{P}(1)\text{-Ga}(2)\text{-P}(2) = 145.6^\circ$. A "side on" view of the molecular core is shown in Figure 2. For comparison, $[\text{Bu}_2^{\text{n}}\text{GaPBu}_2^{\text{t}}]_2$ ^{4a} and $[\text{Bu}_2^{\text{t}}\text{GaP}(\text{H})(\text{C}_5\text{H}_9)]_2$ ²² have planar Ga_2P_2 rings.

Gallium-phosphorus distances (in increasing order) are $\text{Ga}(2)\text{-P}(1) = 2.479(3)\text{\AA}$, $\text{Ga}(1)\text{-P}(1) = 2.482(3)\text{\AA}$, $\text{Ga}(2)\text{-P}(2) = 2.488(3)\text{\AA}$ and $\text{Ga}(1)\text{-P}(2) = 2.512(3)\text{\AA}$ (average = $2.490 \pm 0.015\text{\AA}$). These Ga-P distances are longer than the Ga-P distance in gallium-phosphide²³ of 2.360\AA , in $\text{Ga}[\text{P}(\text{H})\text{Ar}]_3$ (Ar =

2,4,6-Bu^t₃C₆H₂)^{4a} of 2.34(1) and in [Li(THF)₄][Ga(PPh₂)₄]²⁴ of 2.409(7)Å but comparable to the distances in [Buⁿ₂GaPBu^t₂]₂^{4a} of 2.468(4)Å to 2.483(5)Å and in [Bu^t₂GaP(H)(C₅H₉)]₂²² of 2.451(1)Å. The gallium-C(neopentyl) distances (in order) are Ga(1)-C(21) = 1.996(12)Å, Ga(1)-C(11) = 1.997(12)Å, Ga(2)-C(41) = 2.002(11)Å and Ga(2)-C(31) = 2.016(12)Å (average = 2.003±0.009Å).

Angles within the Ga₂P₂ ring are acute at gallium (P(1)-Ga(1)-P(2) = 81.33(11)° and P(2)-Ga(2)-P(1) = 81.88(11)°) and obtuse at phosphorus (Ga(1)-P(1)-Ga(2) = 93.11(11) and Ga(2)-P(2)-Ga(1) = 92.16(11)°). It seems probable that the buckling of the Ga₂P₂ ring results from steric interactions between the bulky Me₃CCH₂ and/or PPh₂ ligands. The tetrahedral geometry at the gallium(III) atoms is irregular. The small P-Ga-P angles have already been noted. There are some angles substantially increased from the ideal tetrahedral value of 109.47°. Noteworthy are the following: (a) angles between the neopentyl ligands - C(11)-Ga(1)-C(21) = 124.35(50)° and C(31)-Ga(2)-C(41) = 121.98(49)°, and (b) one angle, at each gallium atom, between a neopentyl and a diphenylphosphido ligand - P(2)-Ga(1)-C(21) = 121.41(37)° and P(2)-Ga(2)-C(31) = 128.61(37)°. The former require no further explanation; the latter involve neopentyl ligands on the crowded "hinged" surface of the Ga₂P₂ core (i.e., the upper surface of Figure 2).

Within the neopentyl ligands, the Ga-C(α)-C(β) angles are expanded from the normal tetrahedral value (a feature general to metal-neopentyl complexes): Ga(1)-C(11)-C(12) = 122.5(8)°, Ga(1)-C(21)-C(22) = 124.2(9)°, Ga(2)-C(41)-C(42) = 124.2(8)° and Ga(2)-C(31)-C(32) = 124.5(9)° (average = 123.9±0.9°). All other distances and angles are within the normal ranges.

Crystals of bisneopentylindium diphenylphosphide are composed of discrete trimeric units of composition [(Me₃CCH₂)₂InPPh₂]₃, separated by normal van der Waal's distances. The molecules lie on crystallographic

three-fold axes and have crystallographically-imposed C_3 symmetry. A single molecule thus encompasses the equipoints x,y,z ; $-y,x-y,z$; and $y-x,-x,z$. The molecular structure is illustrated in Figure 3. Distances and angles are compiled in Tables 6 and 7. Figure 4 provides a stereoscopic view of the molecule.

The In_3P_3 core of the molecule takes up the classical chair conformation (similar to cyclohexane) with strict C_3 symmetry and approximate C_{3v} symmetry. The two independent In-P bond lengths are In-P = 2.677(1)Å and In-P($-y,x-y,z$) = 2.699(2)Å and the two independent intraring angles are P-In-P($-y,x-y,z$) = 100.78(4)° and In-P-In($y-x,-x,z$) = 125.13(5)°. These In-P distances may be compared to the In-P bond distances in $[(Me_3SiCH_2)_2InPPh_2]_2$ ⁶ of 2.664(2)Å and 2.643(2)Å for Molecule "A" and of 2.659(2)Å and 2.632(2)Å for Molecule "B", in $(Me_2InPBu_2^t)_2$ ⁵ of 2.637(4) and 2.656(4)Å, in indium phosphide^{23,25} of 2.541(3)Å and in $[Li(THF)][In(PPh_2)_4]$ ²⁴ of 2.576Å (average). The In-P distances in the adducts $Me_3In \cdot P(Ph_2)CH_2CH_2(Ph_2)P \cdot InMe_3$ ²⁶ of 2.755(4)Å and $Cl_3In \cdot 2PPh_3$ ²⁷ of 2.723(5) and 2.701(5)Å are longer than in the trimer. However, the bond distance of 2.683(4)Å for $Me_3In \cdot PMe_3$ ²⁶ is comparable. The indium-C(neopentyl) distances are In-C(1) = 2.182(6)Å and In-C(6) = 2.210(7)Å (average = 2.196Å).

Both the indium and phosphorus atoms have distorted tetrahedral environments. The organic groups peripheral to the In_3P_3 core appear to be crowded, but the most dramatic distortions involve the neopentyl groups. The C-In-C angles are greatly distorted from a regular tetrahedral angle, to the value C(1)-In-C(6) = 143.11(26)°. The In-C(α)-C(β) angles for the

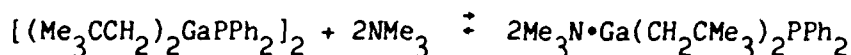
neopentyl ligands are similar to those in the corresponding gallium-phosphorus compound, with $\text{In-C(1)-C(2)} = 125.25(45)^\circ$ and $\text{In-C(6)-C(7)} = 123.89(52)^\circ$.

Other features of the interatomic parameters are normal, with $\text{P-C} = 1.840(6)\text{--}1.850(6)\text{\AA}$, $\text{C-C(phenyl)} = 1.360(1)\text{--}1.397(1)\text{\AA}$ (average = $1.383 \pm 0.011\text{\AA}$) and $\text{C-C(neopentyl)} = 1.478(13)\text{--}1.549(9)\text{\AA}$ (average = $1.516 \pm 0.023\text{\AA}$).

The cryoscopic molecular weight measurements in benzene solution permit comparisons of the degrees of association of the compounds in solution and in the solid state. The gallium-phosphorus derivative is a dimer in solution whereas the indium compound is a monomer-dimer equilibrium mixture as indicated by the concentration dependence of the molecular weight as well as of the ^1H and ^{31}P NMR spectral data. The observed molecular weight for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ did not change significantly with concentration and only one line was observed in the ^{31}P NMR spectrum over the concentration range of 0.024–0.403 m. In contrast, as solutions of $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$ were diluted, the molecular weight decreased and the relative intensities of the two ^{31}P NMR lines changed.⁶ These observations suggest that thermodynamic factors such as solvation energies and entropic effects rather than kinetic factors influence significantly the degree of association of R_2MER_2 compounds. X-ray structural studies cannot be used with any degree of reliability to predict the degree of association of the amphoteric group 13–15 compounds of this type in solution. Since the corresponding trimethylsilylmethyl derivatives,⁶ $(\text{Me}_3\text{SiCH}_2)_2\text{MPPh}_2$ ($\text{M} = \text{Ga}, \text{In}$) were monomer-dimer equilibrium mixtures, the data suggest the neopentyl substituent is a stronger electron withdrawing group than the trimethylsilylmethyl group and the metal is a correspondingly better Lewis acid.^{12,13}

The ^1H NMR spectrum of $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ in benzene (0.024-0.403 molal) revealed a singlet at 1.10 ppm for the methyl protons of the neopentyl group and a triplet at 1.39 ppm for the methylene protons of the neopentyl group with no dependence on concentration. The triplet with the coupling constant value $^3J_{\text{PGaCH}} = 3.6$ Hz was due to phosphorus-31 coupling by two phosphorus atoms adjacent to a gallium atom as in the dimer. ^{31}P NMR spectral studies in the same concentration range as the ^1H NMR studies revealed only a singlet at -25.0 ppm. The molecular weight data suggest that this line is due to the dimer. Some limited data in the literature⁶ for ^{31}P NMR spectra of compounds of the type $\text{R}_2\text{MER}'_2$ suggested a relationship to exist between δ and the degree of association. For example, the spectra for $(\text{Me}_3\text{SiCH}_2)_2\text{GaPPh}_2$ and $(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2$ ⁶ have lines for the monomer and dimer at -27, -40 and -29, -50 ppm, respectively. This relationship would have erroneously suggested that $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$ might be monomeric in solution. Thus, ^{31}P NMR spectra data should not be used to predict the degree of association of the compound in solution.

The gallium phosphide, $(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2$ was reacted with the Lewis bases Et_2O , THF and NMe_3 and with the Lewis acid $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ in order to determine if the phosphide was a Lewis acid or base. No stable (isolable) room temperature adducts were formed. However, the ^{31}P NMR spectra suggested that only NMe_3 was a sufficiently strong base to form an equilibrium mixture with an apparent adduct. The simplest possible adduct would be $\text{Me}_3\text{N}\cdot\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$ but other adducts involving partially dissociated dimers and rapid equilibria cannot be discounted. The ^{31}P NMR



spectrum of a mixture of $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ and NMe_3 in a one to ten mole ratio, respectively, in benzene solution had resonances at -25.1 ppm ($[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$) and -43.7 ppm with relative intensities of 4.21 to 1.00, respectively. The resonance at -43.7 ppm might be due to the adduct, $\text{Me}_3\text{N}\cdot\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{PPh}_2$. Previously, the compounds $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$, $(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2$ and $(\text{Me}_3\text{SiCH}_2)_2\text{GaPPh}_2$ had been observed by ^{31}P NMR spectra to form apparently similar adducts with NMe_3 .⁶

Acknowledgement. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co.

Supplementary Material Available. Anisotropic thermal parameters, calculated hydrogen atom positions, additional C-C bond lengths and angles and an F_o/F_c listing for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$ and $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$ (pages total). For ordering information, see any current masthead page.

References

1. Cowley, A.H.; Jones, R.A. *Angew. Chem. Int. Ed. Engl.* 1989, 28, 1208 and references therein.
2. Byrne, E.K.; Parkanyi, L.; Theopold, K.H. *Science (Washington)* 1988, 241, 332.
3. Higa, K.T.; George, C. *Organometallics* 1990, 9, 275.
4. a) Arif, A.M.; Benac, B.L.; Cowley, A.H.; Geerts, R.L.; Jones, R.A.; Kidd, K.B.; Power, J.M.; Schwab, S.T. *J. Chem. Soc. Chem. Commun.* 1986, 1543.
b) Arif, A.M.; Benac, B.L.; Cowley, A.H.; Jones, R.A.; Kidd, K.B.; Nunn, C.M. *New J. Chem.* 1988, 12, 553.
5. Aitchison, K.A.; Backer-Dirks, J.D.J.; Bradley, D.C.; Faktor, M.M.; Frigo, D.M.; Hursthouse, M.B.; Hussain, B.; Short, R.L. *J. Organometal. Chem.* 1989, 366, 11.
6. Beachley, O.T., Jr.; Kopasz, J.P.; Zhang, H.; Hunter, W.E.; Atwood, J.L. *J. Organometal. Chem.* 1987, 325, 69.
7. a) Maury, F.; Constant, G. *Polyhedron* 1984, 3, 581.
b) Maury, F.; Combes, M.; Constant, G.; Cartes, R.; Renucci, J.B. *J. Phys., Colloq.* 1982, 43, C1.
8. Pitt, C.G.; Purdy, A.P.; Higa, K.T.; Wells, R.L. *Organometallics* 1986, 5, 1266.
9. Beachley, O.T., Jr.; Coates, G.E. *J. Chem. Soc.* 1965, 3241.
10. Chen, J.C.; Chen, W.K.; Liu, P.L.; Maloney, J.D.; Beachley, O.T., Jr. *SPIE (Microelectronic Materials)* 1988, 877, 21.
11. Liu, P.L.; Beachley, O.T., Jr.; Maloney, J.D. Unpublished observations.
12. Beachley, O.T., Jr.; Pazik, J.C. *Organometallics* 1988, 7, 1516.

13. Beachley, O.T., Jr.; Spiegel, E.F.; Kopasz, J.P.; Rogers, R.D.
Organometallics 1989, 8, 1915.
14. Beachley, O.T., Jr.; Tessier-Youngs, C. Organometallics 1983, 2, 796.
15. Shriver, D.F.; Drezdson, M.A. "The Manipulation of Air Sensitive Compounds", 2nd Edition, John Wiley, New York, 1986, p 38.
16. Churchill, M.R.; Lashewycz, R.A.; Rotella, F.J. Inorg. Chem. 1977, 16, 265.
17. International Tables for X-Ray Crystallography, Volume 4, Kynoch Press, Birmingham, England, 1974, pp 99-101.
18. Ibid, pp 149-150.
19. Germain, G.; Main, P.; Woolfson, M.M. Acta Cryst. Sect. A, 1971, A27, 368.
20. Churchill, M.R. Inorg. Chem. 1973, 12, 1213.
21. International Tables for Crystallography, Volume 1, Kynoch Press, Birmingham, England, 1965, pp 252-3.
22. Heaton, D.E.; Jones, R.A.; Kidd, K.B.; Cowley, A.H.; Nunn, C.M.
Polyhedron 1988, 7, 1901.
23. Wyckoff, R.W.G. "Crystal Structures", 2nd Edition; John Wiley, New York, 1963; Vol. 1, p. 108.
24. Carrano, C.J.; Cowley, A.J.; Giolando, D.M.; Jones, R.A.; Nunn, C.M.; Power, J.M. Inorg. Chem. 1988, 27, 2709.
25. Wyckoff, R.W.G. "Crystal Structures", 2nd Edition, John Wiley, New York, 1963; Vol. 4, p 531.
26. Bradley, D.C.; Chudzynska, H.; Faktor, M.M.; Frigo, D.M.; Hursthouse, B.; Hussain, B.; Smith, L. Polyhedron 1988, 7, 1289.
27. Veidis, M.V.; Palenik, G.I. J. Chem. Soc. (D.) Chem. Comm. 1969, 586.

Table 1

Experimental Data for the X-Ray Diffraction Studies of $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$
and $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

(A) Unit Cell Parameters

	Ga dimer	In trimer
Cryst. System	monoclinic	rhombohedral (hexagonal setting)
Space Group	$P2_1/n$ (No. 14, var)	$R\bar{3}$ (No. 148)
\underline{a} , Å	11.076(2)	20.873(5)
\underline{b} , Å	18.996(3)	20.873(5)
\underline{c} , Å	21.753(5)	29.037(4)
$\underline{\alpha}$, deg	90	90
$\underline{\beta}$, deg	100.128(9)	90
$\underline{\gamma}$, deg	90	120
V , Å ³	4505(2)	10956(4)
Z	4(dimers)	6(trimers)
formula	$\text{C}_{44}\text{H}_{64}\text{Ga}_2\text{P}_2$	$\text{C}_{66}\text{H}_{96}\text{In}_3\text{P}_3$
mol. wt	794.3	1326.7
$D(\text{calcd})$, gcm ⁻³	1.17	1.21
Temp.	21°C(294K)	24°C(297K)

(B) Measurement of Intensity Data

Diffractionmeter: Syntex P2₁

Radiation: Mo K α (λ = 0.710730Å)

Monochromator: pyrolytic graphite ($2\theta_m$ = 12.160°), equatorial mode,
assumed 50% perfect/50% mosaic for polarization correction.

Reflections measured: (a) Ga dimer; +h, +k, $\pm l$ for 2θ = 4.5-45.0°; 4757
total reflections, yielding 4398 unique data [$R(I)$ = 4.5%
for 359 groups of averaged data]; (b) In trimer, +h, $\pm k$, $\pm l$
for 2θ = 4.5-45.0°; 10,215 reflections, yielding 3214
unique data [$R(I)$ = 3.1% for averaging of three forms].

Scan type: θ (crystal)- 2θ (counter) at 4.0 deg/min in 2θ from [$2\theta(K\alpha_1) - \Delta$]°
to [$2\theta(K\alpha_2) + \Delta$]°. (Δ = 1.0° for Ga dimer and 0.8° for In
trimer).

Backgrounds: stationary crystal and counter at each end of the 2θ scan,
each for one-quarter of total scan time.

Standard reflections: three approximately mutually orthogonal reflections
collected after each batch of 97 data; substantial decay was
observed and corrected for the Ga dimer (see text); neither
significant fluctuations nor decay were observed for the In
trimer.

Absorption corrections: (a) Ga dimer; μ = 13.6 cm⁻¹, data corrected
empirically by interpolation in 2θ and ϕ between transmission
curves (ψ -scans) of four close-to-axial reflections (T_{min}/T_{max}
= 0.75): (b) In trimer; μ = 10.3 cm⁻¹; 5 close-to-axial ψ -
scans (T_{min}/T_{max} = 0.87).

Table 2

Final Positional Parameters for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$.

ATOM	X	Y	Z	B(Å ²)
Ga(1)	1.02966(11)	0.22446(7)	0.08152(6)	
Ga(2)	0.78146(11)	0.28559(7)	0.15467(6)	
P(1)	1.00824(26)	0.28097(17)	0.18195(13)	
P(2)	0.81608(27)	0.18406(16)	0.08761(15)	
C(11)	0.9953(10)	0.28706(64)	0.00675(55)	
C(12)	1.0803(12)	0.34903(66)	-0.00361(57)	
C(13)	1.2075(16)	0.3275(10)	0.0005(12)	
C(14)	1.0725(17)	0.40711(80)	0.04283(73)	
C(15)	1.0364(16)	0.38142(89)	-0.06826(69)	
C(21)	1.1727(11)	0.15922(63)	0.09996(58)	
C(22)	1.1981(12)	0.10018(75)	0.05710(70)	
C(23)	1.1127(19)	0.0397(11)	0.0630(12)	
C(24)	1.1632(26)	0.1190(12)	-0.0111(11)	
C(25)	1.3219(15)	0.0695(10)	0.07321(85)	
C(31)	0.7012(11)	0.28636(67)	0.23095(56)	
C(32)	0.6005(11)	0.23435(64)	0.24255(57)	
C(33)	0.5020(15)	0.2282(10)	0.18369(76)	
C(34)	0.5387(14)	0.2638(10)	0.29426(76)	
C(35)	0.6494(13)	0.16142(79)	0.26290(67)	
C(41)	0.7527(10)	0.36213(57)	0.09051(55)	
C(42)	0.6715(12)	0.42639(72)	0.09468(65)	
C(43)	0.6674(12)	0.47328(75)	0.03706(75)	
C(44)	0.5425(15)	0.4057(10)	0.0985(10)	
C(45)	0.7246(18)	0.47004(88)	0.15086(91)	
C(51)	1.0623(10)	0.22182(57)	0.24583(48)	2.94(22)
C(52)	0.9837(13)	0.17843(74)	0.27149(65)	5.49(33)
C(53)	1.0254(16)	0.13348(88)	0.32071(79)	7.71(43)
C(54)	1.1454(15)	0.12773(81)	0.34617(70)	6.72(38)
C(55)	1.2231(16)	0.17166(95)	0.32176(81)	8.04(44)
C(56)	1.1841(14)	0.21743(78)	0.27247(69)	6.32(35)
C(61)	1.0882(10)	0.36287(56)	0.20834(48)	2.94(24)
C(62)	1.2072(13)	0.37432(74)	0.20164(63)	5.54(33)
C(63)	1.2660(14)	0.43885(88)	0.22076(74)	7.16(40)

C(64)	1.2012(15)	0.48809(89)	0.24673(77)	7.57(42)
C(65)	1.0874(15)	0.47867(87)	0.25485(75)	7.61(42)
C(66)	1.0266(12)	0.41331(70)	0.23558(62)	4.96(31)
C(71)	0.7904(10)	0.09465(57)	0.11534(52)	3.17(25)
C(72)	0.6772(11)	0.06088(62)	0.09699(55)	4.01(28)
C(73)	0.6590(12)	-0.00615(68)	0.12166(60)	4.71(30)
C(74)	0.7491(13)	-0.03894(70)	0.15980(64)	5.38(33)
C(75)	0.8601(13)	-0.00865(76)	0.17856(65)	5.84(34)
C(76)	0.8813(12)	0.05947(69)	0.15643(61)	4.88(31)
C(81)	0.7143(10)	0.18583(56)	0.01223(49)	2.77(23)
C(82)	0.6004(12)	0.21415(66)	0.00525(58)	4.72(29)
C(83)	0.5200(13)	0.21190(78)	-0.05563(69)	6.42(36)
C(84)	0.5617(13)	0.18055(76)	-0.10479(67)	6.05(35)
C(85)	0.6736(14)	0.15230(75)	-0.09742(69)	6.15(35)
C(86)	0.7522(11)	0.15551(65)	-0.03870(57)	4.21(28)

Table 3

Final Positional Parameters for $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

ATOM	X	Y	Z
In	0.11701(2)	0.14304(2)	0.22886(1)
P	0.12440(7)	0.02328(6)	0.20437(5)
C(1)	0.10909(32)	0.11839(33)	0.30234(20)
C(2)	0.16389(37)	0.16965(37)	0.33957(21)
C(3)	0.15905(45)	0.23962(49)	0.34453(30)
C(4)	0.24368(40)	0.19260(45)	0.32519(29)
C(5)	0.14279(63)	0.12899(62)	0.38461(28)
C(6)	0.18572(39)	0.22618(35)	0.17660(26)
C(7)	0.22483(34)	0.30816(31)	0.18468(28)
C(8)	0.17040(49)	0.33198(41)	0.20028(41)
C(9)	0.26433(75)	0.34988(50)	0.14299(37)
C(10)	0.28517(61)	0.32983(57)	0.22049(64)
C(11)	0.14612(26)	0.02720(26)	0.14229(19)
C(12)	0.19021(33)	0.00029(36)	0.12517(20)
C(13)	0.20144(42)	0.00134(46)	0.07767(25)
C(14)	0.16901(39)	0.02692(46)	0.04744(22)
C(15)	0.12496(36)	0.05317(38)	0.06443(22)
C(16)	0.11416(28)	0.05388(30)	0.11171(19)
C(21)	0.21227(27)	0.04577(26)	0.23240(17)
C(22)	0.27871(28)	0.10686(31)	0.21830(20)
C(23)	0.34434(30)	0.12711(37)	0.24138(24)
C(24)	0.34372(34)	0.08806(40)	0.27958(26)
C(25)	0.27963(36)	0.02821(36)	0.29382(26)
C(26)	0.21400(30)	0.00643(30)	0.27020(21)

Table 4

Interatomic Distances (Å) for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$.

(A) Gallium-Phosphorus Distances

Ga(1)-P(1)	2.482(3)	Ga(2)-P(2)	2.488(3)
Ga(1)-P(2)	2.512(3)	Ga(2)-P(1)	2.479(3)

(B) Gallium-Carbon Distances

Ga(1)-C(11)	1.997(12)	Ga(2)-C(31)	2.016(12)
Ga(1)-C(21)	1.996(12)	Ga(2)-C(41)	2.002(11)

(C) Phosphorus-Carbon Distances

P(1)-C(51)	1.805(11)	P(2)-C(71)	1.841(11)
P(1)-C(61)	1.832(11)	P(2)-C(81)	1.820(11)

(D) Neopentyl Carbon-Carbon Distances

C(11)-C(12)	1.548(17)	C(31)-C(32)	1.544(18)
C(12)-C(13)	1.454(22)	C(32)-C(33)	1.533(20)
C(12)-C(14)	1.509(20)	C(32)-C(34)	1.522(21)
C(12)-C(15)	1.534(20)	C(32)-C(35)	1.525(19)
C(21)-C(22)	1.516(19)	C(41)-C(42)	1.528(18)
C(22)-C(23)	1.508(26)	C(42)-C(43)	1.532(21)
C(22)-C(24)	1.510(27)	C(42)-C(44)	1.498(22)
C(22)-C(25)	1.474(22)	C(42)-C(45)	1.508(23)

Table 5

Angles (in deg) for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$.

(A) Angles around the Gallium Atom

P(1)-Ga(1)-P(2)	81.33(11)	P(2)-Ga(2)-P(1)	81.88(11)
P(1)-Ga(1)-C(11)	115.18(35)	P(2)-Ga(2)-C(31)	128.61(37)
P(1)-Ga(1)-C(21)	106.67(37)	P(2)-Ga(2)-C(41)	100.16(34)
P(2)-Ga(1)-C(11)	100.30(35)	P(1)-Ga(2)-C(31)	112.22(36)
P(2)-Ga(1)-C(21)	121.41(37)	P(1)-Ga(2)-C(41)	102.88(34)
C(11)-Ga(1)-C(21)	124.35(50)	C(31)-Ga(2)-C(41)	121.98(49)

(B) Angles around the Phosphorus Atom

Ga(1)-P(1)-Ga(2)	93.11(11)	Ga(2)-P(2)-Ga(1)	92.16(11)
Ga(1)-P(1)-C(51)	109.77(36)	Ga(2)-P(2)-C(71)	118.32(38)
Ga(1)-P(1)-C(61)	121.83(37)	Ga(2)-P(2)-C(81)	112.27(37)
Ga(2)-P(1)-C(51)	113.02(36)	Ga(1)-P(2)-C(71)	120.01(38)
Ga(2)-P(1)-C(61)	117.28(36)	Ga(1)-P(2)-C(81)	112.75(37)
C(51)-P(1)-C(61)	102.17(50)	C(71)-P(2)-C(81)	101.85(51)

(C) Gallium-Carbon-Carbon Angles

Ga(1)-C(11)-C(12)	122.5(8)	Ga(2)-C(31)-C(32)	124.5(9)
Ga(1)-C(21)-C(22)	124.2(9)	Ga(2)-C(41)-C(42)	124.2(8)

(D) Phosphorus-Carbon-Carbon Angles

P(1)-C(51)-C(52)	122.3(9)	P(2)-C(71)-C(72)	120.7(9)
P(1)-C(51)-C(56)	122.0(9)	P(2)-C(71)-C(76)	121.1(9)
P(1)-C(61)-C(62)	121.5(9)	P(2)-C(81)-C(82)	121.7(9)
P(1)-C(61)-C(66)	118.7(9)	P(2)-C(81)-C(86)	119.2(9)

Table 6

Interatomic Distances (Å) for $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

(A) Indium-Phosphorus Distances

In-P	2.677(1)	In-P(-y,x-y,z)	2.699(2)
------	----------	----------------	----------

(B) Indium-Carbon Distances

In-C(1)	2.182(6)	In-C(6)	2.210(7)
---------	----------	---------	----------

(C) Phosphorus-Carbon Distances

P-C(11)	1.850(6)	P-C(21)	1.840(6)
---------	----------	---------	----------

(D) Neopentyl Carbon-Carbon Distances

C(1)-C(2)	1.549(9)	C(6)-C(7)	1.501(9)
C(2)-C(3)	1.520(12)	C(7)-C(8)	1.519(13)
C(2)-C(4)	1.543(13)	C(7)-C(9)	1.478(13)
C(2)-C(5)	1.500(11)	C(7)-C(10)	1.517(18)

Table 7

Interatomic Angles (in deg) for $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

(A) Angles about the Indium Atom

C(1)-In-C(6)	143.11(26)	P-In-P(-y,x-y,z)	100.78(4)
P-In-C(1)	94.16(17)	C(1)-In-P(-y,x-y,z)	103.84(17)
P-In-C(6)	103.49(20)	C(6)-In-P(-y,x-y,z)	104.28(20)

(B) Angles about the Phosphorus Atoms

C(11)-P-C(21)	103.23(24)	In-P-In(y-x,-x,z)	125.13(5)
In-P-C(11)	110.17(18)	C(11)-P-In(y-x,-x,z)	109.95(18)
In-P-C(21)	99.19(18)	C(21)-P-In(y-x,-x,z)	106.30(18)

(C) Indium-Carbon-Carbon Angles

In-C(1)-C(2)	125.25(45)	In-C(6)-C(7)	123.89(52)
--------------	------------	--------------	------------

(D) Phosphorus-Carbon-Carbon Angles

P-C(11)-C(12)	121.89(44)	P-C(21)-C(22)	120.77(42)
P-C(11)-C(16)	119.08(42)	P-C(21)-C(26)	121.25(43)

CAPTIONS TO FIGURES

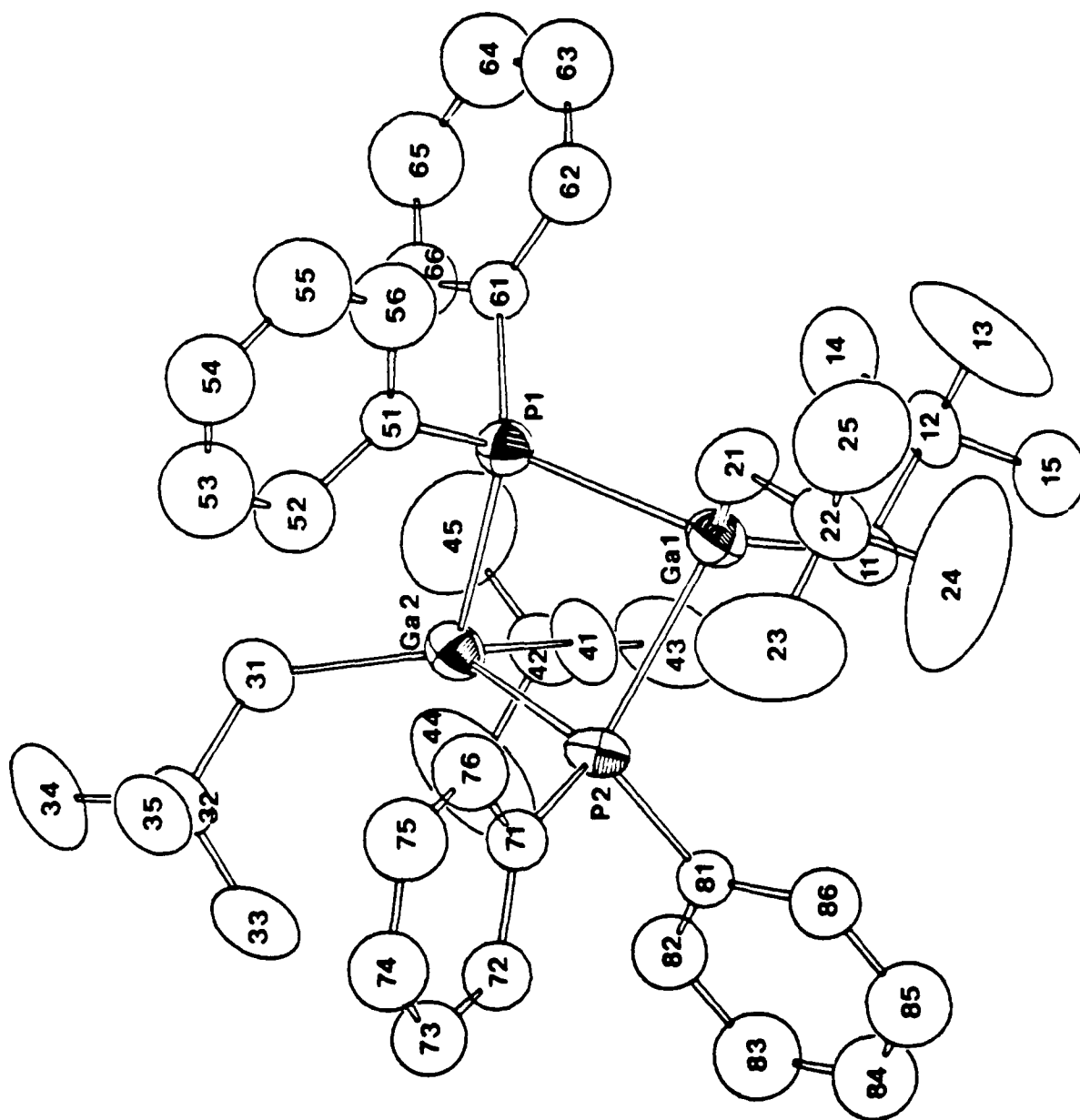
Figure 1. ORTEP diagram for $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$, showing atomic labelling. Carbon atoms are designated by number only.

Figure 2. Side-on view of the molecular core of $[(\text{Me}_3\text{CCH}_2)_2\text{GaPPh}_2]_2$.

Figure 3. ORTEP diagram for $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$. The crystallographic asymmetric unit is stippled.

Figure 4. Stereoscopic view of $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_3$.

FIGURE 1



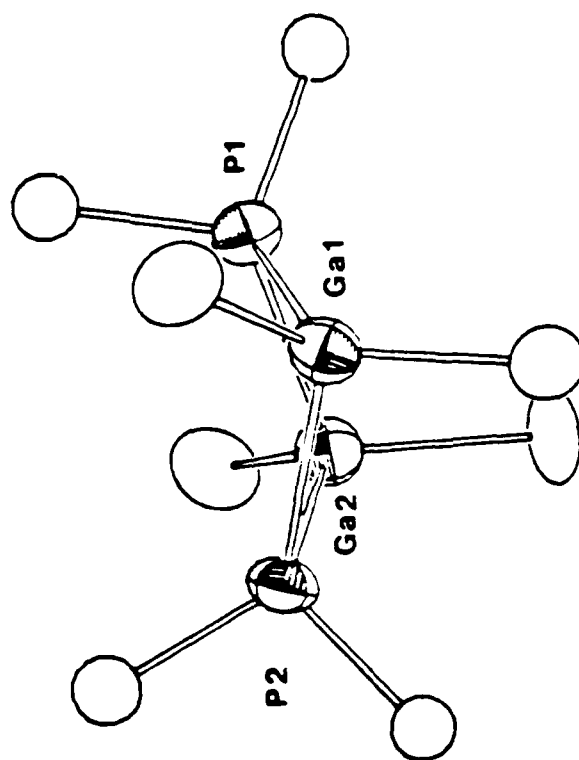


Figure 2

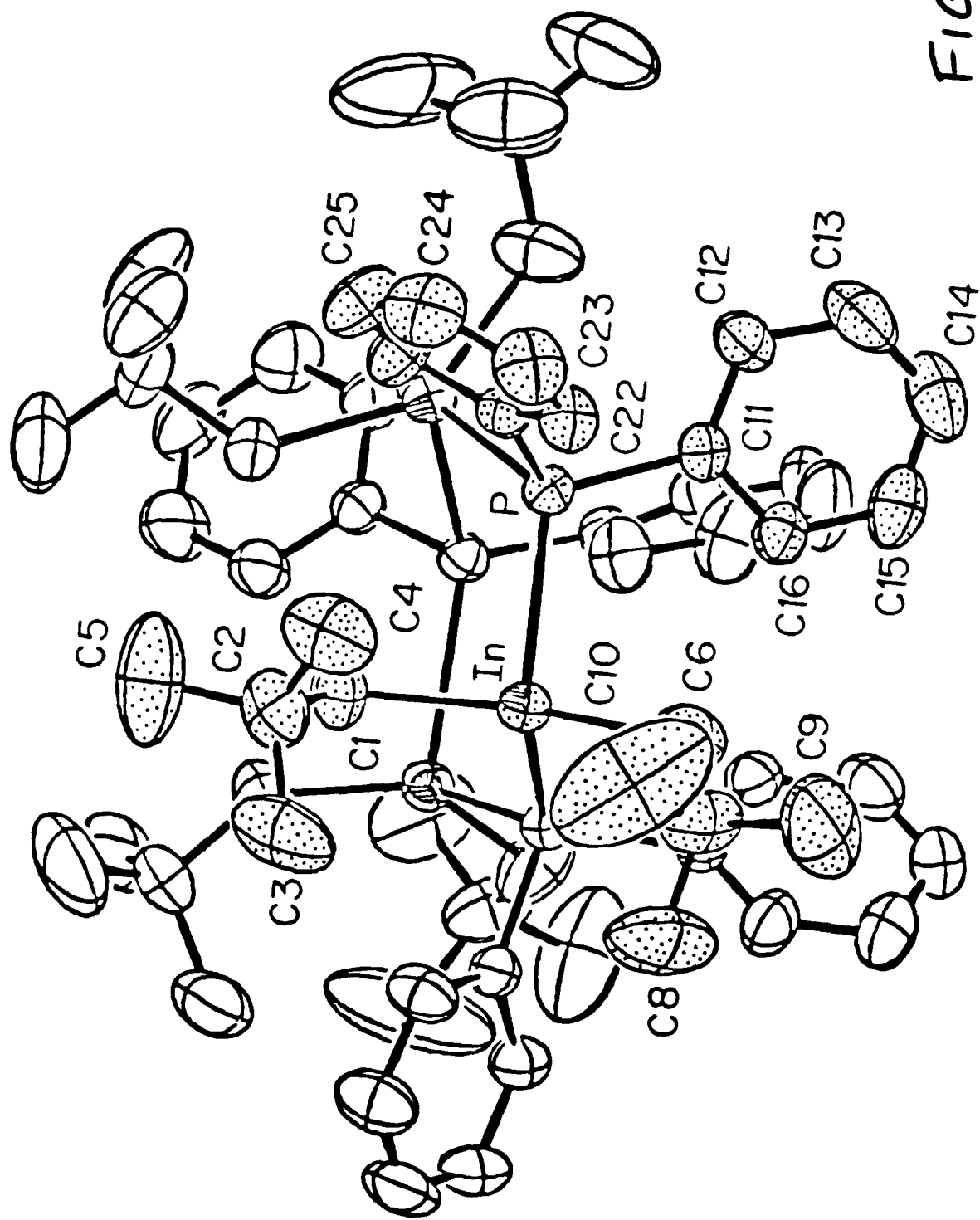
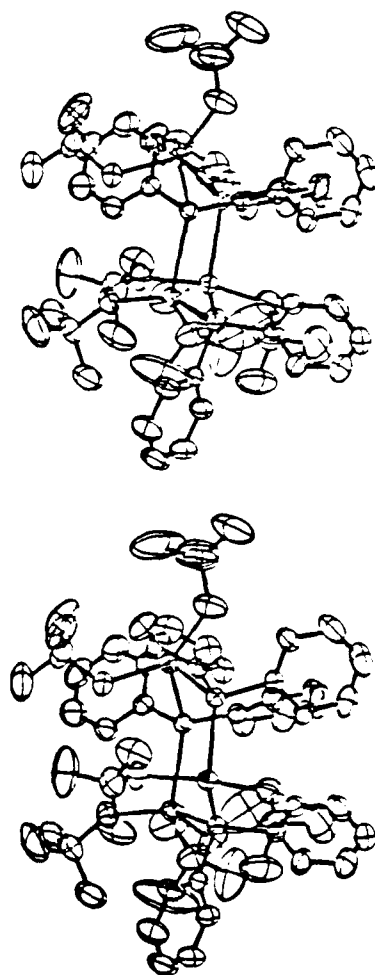


FIGURE 3.

Figure 4



TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

David Taylor Research Center (1)
Dr. Eugene C. Fischer
Annapolis, MD 21402-5067

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering
Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

*Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314*

ENCLOSURE(-)